UDC 666.113.33’28’27:543.42

DETERMINATION OF SODIUM BOROSILICATE BANDS IN THE IR SPECTRUM OF A MULTICOMPONENT BATCH

E. F. Medvedev[1]

Translated from *Steklo i Keramika*, No. 9, pp. 5 – 8, September, 2007.

A borosilicate batch prepared in aqueous medium was investigated by IR spectroscopy. A method was developed for determining the individual sodium borosilicate bands in the presence of the most probable impurities — boric and silicic acids and sodium borate and silicate. The method is based on calculating the absolute degree of difference of the wavenumbers and intensities of the bands. It was found that some of the bands of the five-component batch are indistinguishable with respect to the position in the IR spectrum and the intensity and are unsuitable for analysis. The bands at 653, 1164, 3300, and 3729 cm^{-1} are indistinguishable with respect to the wavenumbers, but differ in the intensities so that they can be conditionally used for identification of sodium borosilicate.

The alkaline borosilicate system is fundamental in the glass industry and in research, but there are extremely few reliable IR spectral data on borosilicates. It is reported in [1] that 15 bands were determined in the IR spectrum of a substance obtained in the borosilicate system, tetragonal $[BO_4]$, 8 bands were determined for $B(OH)_3$, and four closely positioned bands at 664, 670, 672, and 676 cm^{-1} and one band at 926 cm^{-1} were determined for borosilicate. In [2], two bands, at 640 and 920 cm^{-1}, are indicated for the Si – O – B bond in the spectrum of $5ZnO \cdot 15B_2O_3 \cdot 80SiO_2$. These bands can only be assigned to borosilicate if there is a reference spectrum of the individual substance, but there are no such grounds in [1, 2]. For this reason, in view of the limited information (or lack of information), a comparative analysis of the spectra of the individual components of a multicomponent substance would be useful.

The results of identifying the sodium borosilicate bands in a five-component batch by the IR spectral method are reported.

Acids — special-purity silicic and analytically pure orthoboric (henceforth boric) — and analytically pure sodium hydroxide were used for synthesizing the substances in aqueous medium. We first prepared 0.1 liters of sodium hydroxide solution with a concentration of 306 g/liter, 0.1 liter of boric acid solution with a concentration of 89 g/liter, and a suspension of 71.3 g of silicic acid in 0.3 liter of water. The alkaline solution was added to the suspension while stirring and heating in a MM-5 magnetic stirrer with a P-1 proportioner until it totally dissolved. The silicate solution was cooled to room temperature and mixed with the boric acid solution. The sodium borosilicate solution was dried in a polymer tray in ambient conditions for natural evaporation of the water. Then the sodium silicate solution was prepared again. A sodium borate solution was prepared separately by mixing 0.1 liter of boric acid solution with a concentration of 89 g/liter with 0.025 liter of sodium hydroxide solution with a concentration of 116 g/liter. The silicate and borate solutions were dried in the same way as the borosilicate solution.

The IR spectra of the samples of these substances were recorded in the diffuse reflection mode in the 4000 – 400 cm^{-1} region with resolution of 4 – 8 cm^{-1}. A Sartogosm balance was used to sample 0.01 g of each batch with an accuracy of ±0.02 mg, and 0.3 g of potassium bromide was added to each one. The mixtures were ground in a vibration mill for 1 min (grinding bodies — steel ShX15 balls) and then placed in the diffuse reflection module of a Nexus IR Fourier spectrometer. Samples of the initial components — boric and silicic acids, and the intermediate products of synthesis — sodium borate and silicate, were prepared similarly. The spectra of the batch and its components are shown in Fig. 1.[2] The parameters of the bands in the IR spectra of sodium borosilicate NaBSi, borate, NaB, and silicate, NaSi, and boric, HB, and silicic, HSi, acids are reported in Table 1.

[1] Russian Federal Nuclear Center – All-Russia Research Institute of Experimental Physics (RFNC – ARIEP), Sarov, Nizhny Novgorod Oblast, Russia.

[2] The data on IR spectroscopy were provided by A. Sh. Komarevskaya (deceased).

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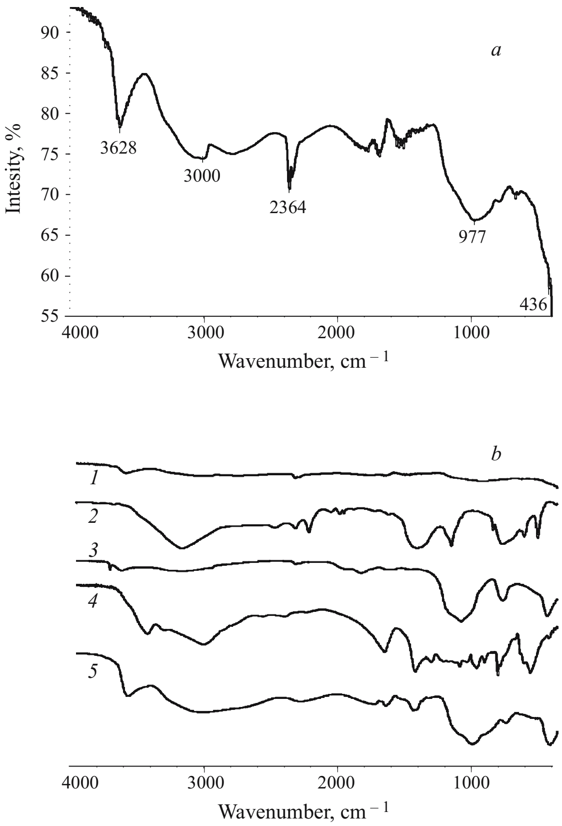

Fig. 1. IR spectra of the substance obtained in the alkaline borosilicate system, initial components, and intermediate products of synthesis: *a*) spectrum of sodium borosilicate batch; *b*) spectra of substances investigated: *1*) target product of synthesis; *2* and *3*) boric and silicic acids; *4* and *5*) sodium borate and silicate.

The SiO_2:H_2O mass ratio (%) in the “silicic acid” reagent was determined with existing methods [3, 4][3] and was 80 : 20 (theoretically, 77 : 23, weight loss on calcination within the limits of 20 – 28% is acceptable), i.e., $SiO_2 : H_2O \equiv H_2SiO_3$.

With few exceptions, the IR spectrum of the borosilicate batch (see Fig. 1*a*) consists of a multitude of narrow bands with sharp peaks that formed complex and basically asymmetric contours in the regions of 750 – 400, 2000 – 1250, 2400 – 2250, 4000 – 3450 cm^{-1}; the regions at 1250 – 700, 2940 – 2450, and 3450 – 2940 cm^{-1} are diffuse, but slightly broadened. This type of spectrum indicates the well-formed crystal structure of the substance. The fine structure of the bands was revealed due to the high resolution provided by the technical capabilities of the Nexus IR-Fourier spectrometer (it is necessary to note that such spectra are not published in the available literature).

The shape of the bands of stretching and deformation vibrations of water at 4000 – 3450, 3450 – 2940, and 1700 – 1600 cm^{-1} indicates that it exists in two forms: in the form of OH groups — crystallization water which is structurally

[3] The analysis with the method from [3] was performed by E. G. Orlikov and I. V. Astakhov, and the analysis with the method from [4] was conducted by E. F. Medvedev.

TABLE 1

Band parameters*					
HBSi	NaB		HB	NaSi	HSi
436/100	462/59	1386/81	409/3	458/100	420/70
453/98	469/59	1393/81	418/7	566/71	478/91
653/73	503/60	1414/82	462/1	785/76	524/61
669/75	531/67	1428/83	548/80	868/81	550/56
794/76	579/91	1448/86	599/35	959/91	566/53
869/80	605/97	1459/93	650/75	1004/99	679/40
977/83	653/87	1545/95	676/66	1037/100	729/42
1036/79	677/77	1559/56	746/82	1130/89	764/44
1121/73	726/60	1572/52	815/93	1363/49	811/67
1164/69	772/73	1634/49	883/61	1392/51	989/51
1379/47	800/78	1641/50	938/28	1421/20	1034/82
1521/54	830/89	1650/54	1015/21	1453/61	1050/88
1684/58	849/100	1662/58	1062/21	1477/63	1086/95
1772/56	883/75	1690/61	1119/56	1580/51	1123/100
2336/59	947/86	1700/73	1230/75	1686/57	1143/96
2343/60	1005/92	1717/73	1285/88	1714/20	1180/91
2364/64	1021/89	1731/70	1450/100	1767/55	1200/88
3000/54	1062/82	2110/67	1662/28	2371/49	1264/61
3050/59	1079/85	2271/28	1763/18	3294/55	1293/30
3300/44	1097/84	2379/30	1927/15	3469/37	1350/23
3571/40	1131/80	2442/30	1998/23	3613/47	1507/16
3628/47	1162/86	2498/35	2029/26		1750/14
3657/44	1195/96	2605/33	2095/22		1804/16
3724/14	1217/85	2952/34	2259/66		1869/21
3729/16	1253/85	3048/56	2359/58		1937/14
	1269/83	3339/56	2514/55		1992/14
	1343/88	3467/50	2677/52		2264/3
		3500/54	2950/62		2331/2
			3209/100		2376/3
			3500/34		3198/17
			3721/4		3649/17
			3829/2		3668/16
					3746/16

* Wavenumber, cm^{-1}/intensity, %.

bound with a component; and in molecular form — coordination water [5]. Considering the method of synthesizing the substance in aqueous medium followed by drying without heat treatment, we can hypothesize that molecular water was present in crystal hydrates.

In comparing the spectral data (see Fig. 1*b* and Table 1) for sodium borosilicate (the arbitrary nature of calling the substance “sodium borosilicate” should be noted, since we know nothing about the ratio of the elements Na, B, Si, and O in its molecule), acids, and salts, it is not difficult to see that some of the bands coincide or are difficult to distinguish

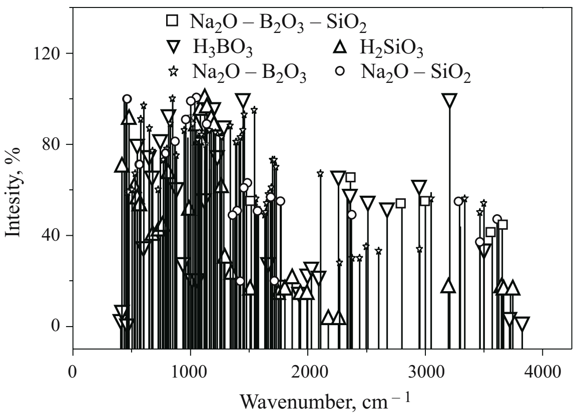

Fig. 2. Line spectrogram of the compared substances.

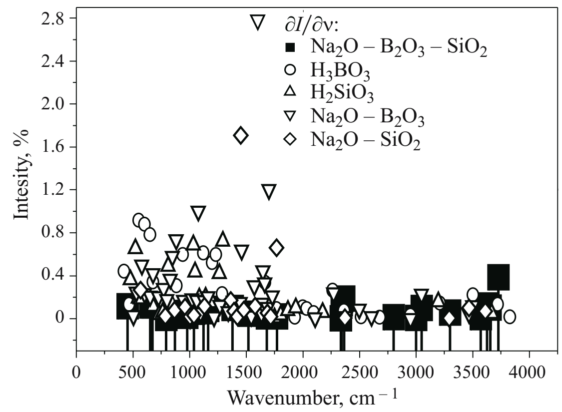

Fig. 3. Determination of the regions of the critical spectral bands of the compared substances and their boundaries with respect to the first derivative $(\partial I/\partial \nu)_i$.

due to their too close position. This is most graphically seen in the line spectrogram (Fig. 2).

We will call such bands "critical." The first derivatives $\partial I/\partial \nu$ (I is the intensity, %; ν is the wavenumber, cm^{-1}) for each substance and the boundaries sought were determined with the regions of intersection of all five bodies $(\partial I/\partial \nu)_{i=1-5}$ (Fig. 3): 1780 – 450, 3730 – 3050, and 2400 cm^{-1}. Both figures (see Figs. 2 and 3) clearly demonstrate the complexity of determining the sodium borosilicate bands, since boric and silicic acids and sodium borate and silicate can be present as impurities and can mask the bands of the target product of synthesis in the overall IR spectrum.

The suitability of the critical bands for identifying sodium borosilicate in the presence of boric and silicic acids and sodium borate and silicate is indicated in Table 2. The absolute degree of difference Δ_p (%) with respect to parameters p (wavenumber ν and intensity I: Δ_ν, Δ_I) was calculated for the critical bands with the general equation

$$\Delta_p = \left| 100 - \frac{100 p_{\min}}{p_{\max}} \right|,$$

where the subscripts "min" and "max" designate the smallest and largest parameters of the compared bands.

In the ideal case, the parameters of the bands should differ by $\Delta_p = 100\%$, but for the critical bands, this condition, as demonstrated, is not satisfied. We agreed to consider that the bands are indistinguishable and unsuitable for identifying substances in a multicomponent batch if the degree of difference $\Delta_p \le 10\%$; if $\Delta_p > 10\%$ for one of them, the bands can be conditionally used; and finally, the bands can always be used for IR analysis when $\Delta_p > 10\%$ for both parameters.

Examples of using the equation for determining Δ_p are given below. The band at $\nu = 794$ cm^{-1} with $I = 76\%$ was selected in the IR spectrum of NaBSi and its parameters were compared with the parameters of the bands at $\nu = 800$ cm^{-1} with $I = 78\%$, at $\nu = 815$ cm^{-1} with $I = 93\%$, at $\nu = 785$ cm^{-1} with $I = 76\%$, and at $\nu = 811$ cm^{-1} with $I = 67\%$ from the spectra of NaB, HB, NaSi, and HSi, respectively (see Table 1).

$$\Delta_\nu = \left| 100 - \frac{100 \times 794}{800} \right| = 0.75\% < 10\%$$

based on the wavenumber ν, the bands of NaBSi and NaB are indistinguishable;

$$\Delta_I = \left| 100 - \frac{100 \times 76}{78} \right| = 2.56\% < 10\%$$

based on the intensity, the bands are also indistinguishable.

Conclusion: in the overall IR spectrum, the bands of sodium borosilicate and borate are indistinguishable, so that they cannot be used for identifying the substances.

$$\Delta_\nu = \left| 100 - \frac{100 \times 794}{815} \right| = 2.58\% < 10\%$$

based on the wavenumber ν, the bands of NaBSi and HB are indistinguishable;

$$\Delta_I = \left| 100 - \frac{100 \times 76}{93} \right| = 18.28\% > 10\%$$

the bands can be distinguished by the intensity.

Conclusion: The bands of borosilicate and boric acid are indistinguishable with respect to the position in the IR spectrum but can be distinguished by the intensity and the bands can consequently be conditionally used for identifying these substances.

$$\Delta_\nu = \left| 100 - \frac{100 \times 785}{794} \right| = 1.13\% < 10\%$$

the bands of NaBSi and NaSi cannot be distinguished with the wavenumber ν;

TABLE 2

Band in spectrum of NaBSi	Absolute degree of difference of the parameters of the band sin the compared spectra								Suitability of band
	NaBSi – NaB		NaBSi – HB		NaBSi – NaSi		NaBSi – HSi		
	Δ_ν	Δ_I	Δ_ν	Δ_I	Δ_ν	Δ_I	Δ_ν	Δ_I	
453/98	1.9	39.8	1.9	99.0	1.1	2.0	None	None	–
653/73	0.0	16.1	None	None	None	None	″	″	±
669/75	1.2	2.6	1.0	12.0	″	″	1.5	46.7	–
794/76	0.7	2.6	2.6	18.3	″	″	2.1	11.8	–
869/80	None	None	None	None	0.1	1.2	None	None	–
1036/79	″	″	″	″	0.1	21.0	″	″	–
1121/73	0.9	8.7	0.2	23.3	0.8	18.0	0.2	27.0	–
1164/69	0.8	19.8	None	None	None	None	None	None	±
1379/47	0.5	42.0	″	″	0.5	4.1	″	″	–
1684/58	0.3	4.9	″	″	0.1	1.7	″	″	–
1772/56	None	None	0.5	67.9	0.3	1.8	1.8	71.4	–
2336/59	″	″	None	None	None	None	0.2	97.0	±
2343/60	″	″	0.7	9.3	0.3	23.4	None	None	–
2364/64	″	″	0.2	31.0	None	None	″	″	±
3050/59	0.1	5.1	None	None	″	″	″	″	–
3300/44	None	None	″	″	0.2	20.0	″	″	±
3724/14	″	″	0.2	31.0	None	None	″	″	±
3729/16	″	″	0.2	75.0	″	″	″	″	±

Comments: "None" means the absence of a closely positioned band in the compared spectrum; "–" and "±" mean unsuitability and conditional suitability of the band for identifying sodium borosilicate in the presence of acids and sodium borate and silicate.

$\Delta_I = 0$: the bands can also not be distinguished by the intensity.

Conclusion: the sodium borosilicate and silicate bands cannot be distinguished with the wavenumbers and intensities, so that they cannot be used for identification of the substances.

$$\Delta_\nu = \left| 100 - \frac{100 \times 794}{811} \right| = 2.1\% < 10\%$$

the bands of NaBSi and HSi cannot be distinguished with the wavenumber ν;

$$\Delta_I = \left| 100 - \frac{100 \times 67}{76} \right| = 11.84\% > 10\%$$

the bands can be distinguished based on the intensity.

Conclusion: The borosilicate and silicic acid bands cannot be distinguished by the position in the IR spectrum of the mixture but can be distinguished by the intensity and can consequently be conditionally used for identifying these substances in a batch.

Sodium borosilicate can be determined in the presence of boric and silicic acids based on the presence of a band at $\nu = 794$ cm^{-1} with $I = 76\%$ by considering the intensities of their bands which are close to the band of the determined substance. However, it is impossible to determine in a three-component batch that additionally contains intermediate products of synthesis — sodium borate and silicate — in addition to the borosilicate. It follows from this that if the band of the determined substance in the spectrum cannot be distinguished with ν and I from the corresponding band of even one of the components of the batch, then it cannot be used for the analysis.

The absolute degrees of difference with respect to the wavenumber and intensity were determined by paired comparison of the bands of sodium borosilicate, acids, and salts with the equation for calculation of Δ_p (see Table 2).

It was found by calculation that 11 of the 18 critical bands cannot be distinguished in the spectrum of a batch with impurities of the indicated substances, while 7 bands can be conditionally used for identifying the borosilicate — they differ in intensity, although they are indistinguishable based on the position in the spectrum (see Tables 1 and 2), i.e., the wavenumber is a necessary but insufficient characteristic of the bands in the spectrum. In doubtful cases, their intensity, which is also a necessary but insufficient characteristic, must be considered. As a consequence, six bands in the IR spectrum of a five-component batch can be assigned to

sodium borosilicate bands: 436/100, 977/83, 1521/54, 3571/40, 3628/47, and 3657/44 (wavenumber, cm^{-1}/intensity of band, %). The bands at 3571, 3628, and 3657 cm^{-1} are due to vibrations of structurally bound OH groups in the borosilicate lattice, for example, $–(OH)_2Si – O – B(OH)–$, while the bands at 436, 977, and 1521 cm^{-1} characterize vibrations of atoms in the Si – O – B bond with no OH groups.

The proximity of the bands used in [1] to identify the Si – O – B bond and formation of borosilicate was noted previously. The results of calculating Δ_p with the proposed method casts doubt on the distinguishability of the 676 and 664 cm^{-1} bands in experiment No. 2: $\Delta_{664-676} = 1.8\% < 10\%$, i.e., the bands cannot be distinguished by the position in the spectrum; no data on the intensity and resolution of the spectrometer were given. The spectra of our substances (see Fig. 1) were printed out on a standard sheet of A4 paper, and 15 mm corresponded to 200 cm^{-1} on the abscissa. If this section is set at 100%, then $\Delta_{664-676} = 1.8\%$ will be equivalent to 0.3 mm on the abscissa. It is obvious that the coordinates of the bands indicated in [1] cannot be determined without a large error. In addition, the bands at 670 cm^{-1} (14.52 μm) and 670.5 cm^{-1} (15.09 μm), 664.8 cm^{-1} (15.16 μm) are assigned to $[B(O, OH)_4]$ and $[BO_4]$ tetrahedrons, while the band at 909 cm^{-1} (11 μm) close to 926 cm^{-1} [1] ($\Delta_{909-926} = 1.8\%$) are assigned to stretching vibrations of OH groups. In consideration of the above, the reliability of determining the Si – O – B bonds in [1, 2] is suspect.

A method was thus developed for determining the individual sodium borosilicate bands in the presence of the most probable impurities — boric and silicic acids, sodium borate and silicate. The method is based on a comparative analysis of the IR spectra of the target substance and the associated components and determining the absolute degree of difference of the wavenumbers and intensities.

It was found that some of the bands in the IR spectrum of a five-component batch cannot be distinguished by either the position in the spectrum or the intensity. The bands at 436, 977, 1521, 3571, 3628, and 3657 cm^{-1} can be assigned to individual sodium borosilicate bands. The intensive bands and bands of medium intensity at 653, 1164, 2236, 2364, 3300, and 3729 cm^{-1} can only conditionally be used for identifying the given substance — they differ in intensity from the closely positioned bands of associated impurities.

The wavenumber is not always a necessary and sufficient characteristic of a band and the intensity should be considered a second characteristic in doubtful cases, but it is usually not reported in the literature.

I would like to thank my colleagues at the RFNC – ARIEP A. Sh. Komarevskaya (deceased), E. G. Orlikov, and I. V. Astakhov for their technical assistance.

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